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ABSTRACT

This booklet presents some methods of quantitative chemical analysis currently used in the field of fresh water pollution control. Only those tests that may be performed with little or no special reagents or pieces of equipment are listed. The booklet addresses the following determinations: (1) acidity; (2) alkalinity; (3) chloride; (4) hardness; (5) oxygen dissolved; (6) pH value; (7) phosphate, all forms; (8) solids, suspended; and (9) solids, total. (Author/RH)

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SEMINOLE COUNTY DISTRICT SCHOOL BOARD

SE 024 760

CHEMISTRY FOR POLLUTION CONTROL

DEVELOPED BY
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LAKE HOWELL HIGH SCHOOL
SEMINOLE COUNTY DISTRICT
SCHOOL BOARD

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INTRODUCTION

The purpose of this booklet is to present some of the methods of quantative chemical analysis that are currently being used in the field of fresh water pollution control. There are many books and kits available that describe various means of analysis, but these books and kits provide no standards for comparison to establish the validity of the test.

The need for uniform guidelines was recognized by the U. S. government and resulted in the establishment of the Environmental Protection Agency (EPA) which was charged with setting the guidelines and policing the industries of America. The tests in this booklet are some of those set forth by the EPA as standards and therefore can be used to provide a useful and valid indication of the condition of the water sample.

Because of the complexity of many tests, we shall be concerned only with those that may be performed with little or no special reagents or pieces of equipment. Specifically, this booklet goes into the following determinations: (1) acidity; (2) alkalinity; (3) chloride; (4) hardness; (5) oxygen, dissolved; (6) pH value; (7) phosphate, all forms; (8) solids, suspended; and (9) solids, total.

If any other methods are desired, the user should consult some of the EPA publications, most especially those listed in the bibliography of this booklet.

To the Teacher:

This booklet was originally intended for use as the curriculum for a one semester Chemistry II course, however, in trying to make it as general as possible it has been modified so that an advanced student in either the biological science or chemistry field can perform most of the determinations with a minimum of direct supervision. The booklet has also been modified so that a class may spend as little as one grading period on the material depending upon how much theory is presented by you, the teacher.

The particular determinations chosen are those that are examples of various analytical procedures that are not normally encountered in a Chemistry I program. They are (1) acid-base titrations; (2) gravimetric determinations; (3) a colorimetric determination; and (4) complex-formation titrations.

In most cases only a small amount of theory is presented, just enough to be a starting point for the procedure that follows. If more of the theoretical aspect is desired, any good quantative analytical chemistry book should present enough theory and references to satisfy your requirements. You might begin with Quantative Analytical Chemistry by James S. Fritz and George H. Schenk, Jr., published by Allyn and Bacon, Inc., Boston.

It will be a great benefit to you to read the appendices before beginning the rest of the booklet.

I would appreciate any comments or criticisms and welcome any questions that you might have concerning any topic covered here. Please do not hesitate to contact me if I can be of any help.

Larry Everson
Lake Howell High School
June 1976

ACIDITY

Theory:

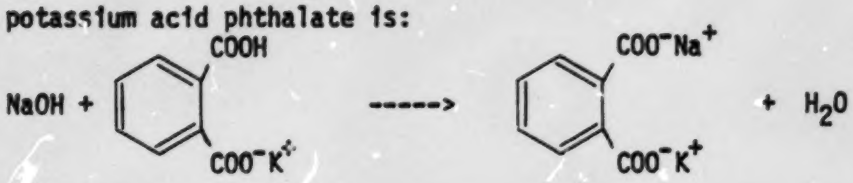
The acidity of a water sample is determined by the use of an acid-base titration. In this method, a stock solution of sodium hydroxide, NaOH, is prepared and standardized by titrating an exactly weighed quantity of a primary standard, preferably potassium acid phthalate (potassium hydrogen phthalate), KHP. A visual indicator or a pH meter is used for detection of the end-point of the titration. Finally, the percentage of acid in the water sample is determined by titration with the standard sodium hydroxide. Once again, a visual indicator or a pH meter is used to determine the titration end-point.

Materials and Reagents:

1. distilled water
2. sodium hydroxide
3. potassium acid phthalate, KHP
4. 1-liter volumetric flask
5. weighing jar or small beaker
6. drying oven
7. phenolphthalein indicator
8. pH meter with electrodes and standard buffers
9. desiccator
10. analytical balance
11. three 125 ml erlenmeyer flasks
12. 25 ml or 50 ml buret
13. magnetic stirrer and stirrer bar (optional)
14. 250 ml beaker

Reactions:

The reaction for the standardization of sodium hydroxide with potassium acid phthalate is:



The reaction for the neutralization of the acids in the water sample depends upon the particular acid in the water, however, the net ionic equation must be: $OH^- + H^+ \longrightarrow H_2O$.

Procedure:

A. Prepare 0.02M (0.02N) sodium hydroxide solution.

1. Boil 1.5 liters of distilled water, let cool, and transfer about 500 ml to a 1-liter volumetric flask.
2. Accurately weigh 0.8 g of NaOH and dissolve it in the volumetric flask.
3. Dilute to volume in the flask.

B. Standardize the 0.02M sodium hydroxide solution.

1. Place about 1 gram of potassium acid phthalate (KHP) in a clean, dry weighing jar or small beaker and dry in an oven at 100°C for at least one hour.
2. After one hour, remove the sample and cool in a desiccator.
3. Accurately weigh (± 0.0001 g) 0.1 to 0.2 grams of the KHP into each of three 125 erlenmeyer flasks, being sure to record the weight of KHP in each flask.
4. Add about 50 ml of distilled water and 2 drops of phenolphthalein to each flask. Swirl to dissolve the KHP.

5. Fill a buret with the 0.02M NaOH solution and record the buret reading.
6. Titrate the solution in the first flask to the first permanent pink color and record the final buret reading.
7. Repeat with the other two samples.

C. Calculate the molarity of the NaOH.

$$\text{Molarity} = \frac{\text{weight of KHP in milligrams}}{(\text{ml NaOH})\ (204.22)}$$

Average the three values for a final result.

D. Determination of the Acidity of the sample.

1. Pour exactly 100.00 ml of the water sample into a 250 ml beaker and add a stirring bar.
2. Titrate with standardized 0.02M NaOH to a pH of 8.3 using a recently standardized pH meter.
3. Calculate acidity as mg/l $CaCO_3$.

$$\text{mg/l } CaCO_3 = \frac{(\text{ml NaOH used})(\text{molarity NaOH})(50{,}000)}{100}$$

ALKALINITY

Theory:

Similar to the determination of the acidity of the water, the alkalinity is determined by an acid-base titration. In this method a solution of 0.01M (0.02N) H_2SO_4 is standardized using the standard sodium hydroxide from the acidity determination. A visual indicator is used to detect the titration end-point. The alkalinity of the water sample is then determined by titration with the standardized sulfuric acid. For this titration a pH meter is used to determine the end of the titration.

Materials and reagents:

1. distilled water
2. standardized sodium hydroxide from the acidity determination
3. 1-liter volumetric flask
4. phenolphthalein indicator
5. pH meter with electrodes and standard buffers
6. three 125 ml erlenmeyer flasks
7. 25 ml or 50 ml buret
8. magnetic stirrer and stirring bar (optional)
9. 1.0 ml pipet graduated by 0.01 ml, with pipet bulb
10. 5.0 ml volumetric pipet
11. 250 ml beaker

Reactions:

The reaction for the standardization of the sulfuric acid is:

$$H_2SO_4 + 2NaOH \text{ -----> } 2H_2O + 2Na^+ + SO_4^{-2}.$$

Like the acidity determination, the reaction for the neutralization of the bases in the water sample depends upon the particular bases present, however, the net ionic equation must be: $OH^- + H^+ \text{-----} > H_2O$.

Procedure:

A. Prepare the 0.01M (0.02N) sulfuric acid.

1. Add about 800 ml of distilled water to a 1-liter volumetric flask.
2. Using a graduated pipet, transfer 0.56 ml of concentrated sulfuric acid to the volumetric flask. **CAUTION: Pipet only with a pipet bulb, and be sure to add the acid to the water very slowly.**
3. Dilute to volume with distilled water.

B. Standardize the 0.01M sulfuric acid.

1. With a 5.0 ml volumetric pipet transfer exactly 5.0 ml of 0.01M H_2SO_4 to each of three 125 ml erlenmeyer flasks.
2. Add about 50 ml of distilled water and three drops of phenolphthalein indicator. Swirl to mix the solution.
3. Fill a buret with standardized 0.02M NaOH and record the buret reading.
4. Titrate the solution in the first flask to the first light pink color that will persist for at least 15 seconds and record the final buret reading.
5. Repeat with the solution in the other two flasks.

C. Calculate the molarity of the sulfuric acid.

$$\text{molarity} = \frac{(2)(\text{amount base used in liters})(\text{molarity of base})}{(0.005)}$$

D. Determine alkalinity of the water sample.

1. Pour exactly 100.0 ml of the water sample into a 250 ml beaker and add a stirring bar.
2. Titrate with 0.01M (0.02N) sulfuric acid to a pH of 4.5 using a recently standardized pH meter.
3. Record the results of the titration.
4. Calculate alkalinity as mg/l $CaCO_3$.

$$\text{mg/l } CaCO_3 = \frac{(\text{ml } H_2SO_4 \text{ used})(\text{molarity } H_2SO_4)(100{,}000)}{100}$$

SOLIDS, TOTAL

Theory:

The total solids are anything that may be dissolved or suspended in the water. This list includes all of the dissolved solids (see dissolved solids determination) and, in addition, includes the solid fraction of sewage and industrial wastes, bottom sediments, and organic material from dead and decaying plants and animals.

Materials and Reagents:

1. Drying oven equipped with thermostatic control capable of maintaining the temperature ± 2°C.
2. Desiccator
3. Analytical balance capable of weighing 0.0001 g.
4. Evaporating dish, 100 ml.

Procedure:

A. Preparation of crucibles and evaporating dishes.

1. All crucibles should be acid cleaned and thoroughly rinsed with distilled water. **CAUTION: Ask your instructor for specific instructions for this step.**
2. Crucibles should be placed in the oven at 105°C, dried for 30 minutes and placed in the desiccator to dry to a constant weight.

B. Determine the Total Solids in ppm.

1. Pour 100.0 ml of a well mixed (shaken rigorously) sample into a weighed evaporating dish.
2. Place the sample in the dish in the oven at 105°C and evaporate the liquid and dry the residue for 24 hours.
3. Place the evaporating dish in the desiccator and allow

it to cool and come to a constant weight.

4. Weigh the crucible to the nearest 0.0001 g and determine the weight of the solids remaining in the dish. Express this weight in milligrams.
5. Calculate the total solids in ppm.

   total solids in ppm = solids remaining in dish, mg X 10.

SOLIDS, SUSPENDED

Theory:

The suspended solids in a water sample are defined as those solids which are retained on a glass fiber filter paper and dried to a constant weight. They include decaying organic matter from plants and animals as well as bottom sediments and those solids from sewage and industrial wastes.

Materials:

1. Drying oven equipped with thermostatic control capable of maintaining the temperature ±2°C.
2. Desiccator.
3. Analytical balance capable of weighing 0.0001 g.
4. Gooch Crucible.
5. Glass fiber filter papers.

Procedure:

A. Preparation of crucibles and evaporating dishes.

1. All crucibles and evaporating dishes should be acid cleaned and thoroughly rinsed with distilled water. **CAUTION: Ask your instructor for specific instructions for this step.**
2. Crucibles should be placed in an oven at 105°C, dried for 30 minutes and placed in a desiccator to dry to a constant weight.
3. Crucibles used for this determination will be prepared with the filter paper in place.

B. Determine the suspended solids in ppm.

1. Filter a 100.0 ml portion of sample through a prepared weighed crucible with the glass fiber filter

paper in position.

2. Place the crucible in the oven at 105°C for one hour.
3. Remove the crucible from the oven and place in the desiccator to cool and come to a constant weight.
4. Weigh the crucible to the nearest 0.0001 g and determine the total suspended solids by the increase in weight. Express this number in milligrams.
5. Calculate total suspended solids in ppm.

   suspended solids in ppm = weight of solids in crucible X 10.

SOLIDS, DISSOLVED

Theory:

The dissolved solids in water include phosphates, nitrates, alkalis, acids, sulfates, iron, magnesium, lead, chloride, zinc, chlorine, chromium, copper sulfur, fluoride, hydrogen sulfide, manganese, mercury, silics and several other minor elements and compounds.

A total dissolved solids (T.D.S.) reading is used as a quick assesment of general water quality. T.D.S. values below 100 ppm are considered oligotrophic while readings over 100 ppm usually indicate an eutrophic condition. Areas with T.D.S. values of 50 ppm have too few nutrients to support reasonable plant and animal populations.

Effluent from sewage treatment plants using secondary treatment usually contain about 300-400 ppm T.D.S.

The U.S. Public Health Service recommends potable water standards of 500 ppm T.D.S., or as high as 1000 ppm.

Dissolved solids are defined as those solids capable of passing through a standard glass fiber filter disc and may be determined by difference of the total solids and suspended solids.

Procedure:

A. Determine the Total Dissolved Solids (T.D.S.)

T.D.S. in ppm = total solids in ppm - suspended solids in ppm.

HARDNESS

Theory:

Water hardness is usually due to bicarbonates, mainly calcium bicarbonate and, to a lesser degree, magnesium bicarbonate. Usually streams and lakes will reflect the geological areas that they are in; thus, in areas largely of gypsum, the water hardness is due to calcium sulfate ($CaSO_4$).

Temporary hardness is the same as carbonate hardness since it can be removed by heating. Permanent hardness is caused by sulfates and chlorides of calcium and magnesium and cannot be removed by heating. Total hardness is the sum of the permanent and temporary hardnesses.

Hardness values are expressed in ppm $CaCO_3$. In order to classify waters, a series of values has been established:

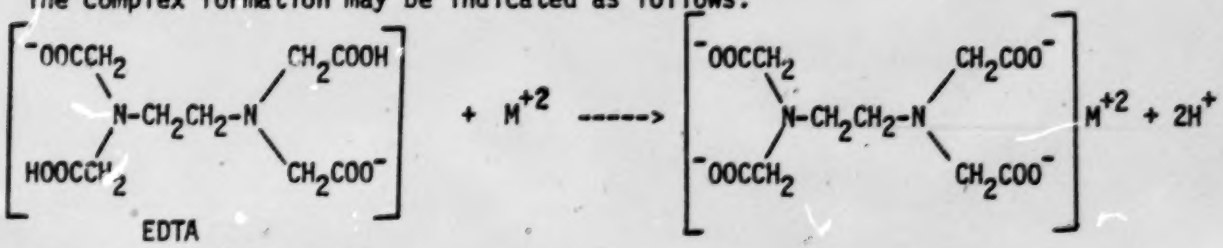
soft water	0 - 60 ppm
moderately hard water	61 - 120 ppm
hard water	121 - 180 ppm
very hard water	over 180 ppm

The U. S. Health Standards for potable water are 200 ppm calcium hardness and 150 ppm magnesium hardness. Total hardness values below 250 ppm are generally acceptable for drinking water. Total hardness values over 500 ppm are hazardous to human health.

The method of analysis for **hardness** is a complex-formation titration. Ethylenediamine tetraacetic acid (EDTA) and its sodium salts form a soluble complex when added to a solution of calcium and magnesium ions. If a small amount of an indicator such as Eriochrome Black T is added to an aqueous solution of calcium and magnesium ions, the solution will become wine red. (The pH must be maintained at 10.0 ± 0.1) If EDTA is added slowly to complex the calcium and magnesium ions, the solution will turn from wine red to blue. The blue color is the end-point of the titration and indicates a complete removal of the calcium and magnesium ions. A limit of 5 minutes is set for the duration of the titration in order to minimize the tendency toward $CaCO_3$ precipitation.

Reactions:

The complex formation may be indicated as follows:



EDTA

$M^{+2} = Ca^{+2}$ or Mg^{+2}.

Reagents:

1. Buffer solution- dissolve 1.179 g disodium salt of ethylene-diamine tetraacetic acid dihydrate and 0.780 g $MgSO_4 \cdot 7H_2O$ or 0.644 g $MgCl_2 \cdot 6H_2O$ in 50 ml distilled water. Add this solution to 16.9 g NH_4Cl and 143 ml concentrated NH_4OH with mixing and dilute to 250 ml with distilled water.

Keep the solution in a plastic or resistant-glass container, tightly stoppered to prevent loss of NH_3 or pickup of CO_2.

Discard the buffer when 1 or 2 ml added to the sample fails to produce a pH of 10.0 ± 0.1 at the end-point of the titration.

2. Indicator- Mix together 0.5 g Eriochrome Black T dye and 100 g NaCl to prepare a dry powder mixture. Indicator formulations tend to deteriorate, especially when exposed to moist air.

3. Standard EDTA titrant, 0.01M.- weigh 3.723 g of the dry EDTA (disodium salt), dissolve in distilled water and dilute to 1 liter. Check the titrant by standardizing against standard calcium solution as described below.

4. Standard Calcium Solution- Weigh 1.0000 g anhydrous calcium carbonate, $CaCO_3$, powder into a 500-ml erlenmeyer flask. Place a funnel in the neck of the flask and add, a little at a time, dilute (50:50) HCl until all of the $CaCO_3$ has dissolved. Add 200 ml distilled water and boil for a few minutes to expel CO_2. Cool, add a few drops of methyl red indicator, and adjust to the intermediate orange color by adding 3N NH_4OH or the dilute HCl. Transfer quantitatively to a 1-liter volumetric flask and fill to the mark with distilled water. This standard solution is equivalent to 1.00 mg $CaCO_3$ per 1.00 ml.

Procedure:

A. Standardization of the EDTA titrant.

Dilute 25.0 ml of standard calcium solution to about 50 ml with distilled water. Add 1-2 ml of buffer solution. Usually 1 ml will be sufficient to give a pH of 10.0 to 10.1. Add a small amount of dry-powder indicator. Add the standard EDTA titrant slowly with continuous stirring until the last reddish tinge disappears from the solution, adding the last few drops at 3-5 second

intervals. The color of the solution at the end-point is blue under normal conditions.

The titration should require about 25 ml of the standard EDTA solution. If exactly 25 ml are used then the EDTA solution is exactly right, if not, then a suitable correction factor must be entered into the final calculation.

$$\text{correction factor, \$} = \frac{25}{\text{ml EDTA required for titration}}$$

B. Determine the hardness of the sample in mg/l $CaCO_3$.

Dilute 25.0 ml of the sample to about 50 ml with distilled water. Add 1-2 ml of buffer solution. Add a small amount of the dry-powder indicator formulation. Add the standard EDTA titrant slowly with continuous stirring until the last reddish tinge disappears from the solution, adding the last few drops at 2-3 second intervals. The color of the end-point is blue.

If less than 15 ml of the EDTA titrant is used, repeat the determination using a larger sample.

C. Calculate the hardness of the water.

$$\text{Hardness as mg/l } CaCO_3 = \frac{A \times \$ \times 1000}{\text{ml sample}}$$

A = ml EDTA required for titration

\$ = correction factor (calculated in part A.)

PHOSPHATES

Theory:

Phosphorus is one of the most important nutrients for plant growth. High phosphate levels usually result in an over abundance of algae and other plant types. When these plants die, their decomposition robs the water of oxygen, thus causing fish kills.

Many scientists believe that this nutrient is the most likely limiting factor for eutrophication, but many scientists also believe that a ratio exists between phosphates and nitrates. In other words, without the proper nitrates, plant growth will not increase even though phosphate levels are high.

It is known that phosphates stimulate nitrogen-fixing blue-green algae. Thus, even if we keep all nitrates out of the water, the blue-green algae will add nitrogen as they decay.

Farm runoff generally contains very little phosphorus. Soils "fix" or hold phosphate ions. The phosphate ions cling to soil particles, thus highly turbid waters containing runoff erosin can have high phosphate levels after heavy rains. The ions diffuse from the soil particles into the surrounding water raising phosphate counts of the water.

Generally, phosphate levels higher than 0.015 ppm in organic phosphorus are considered to be high. In the phosphate rich regions of Florida near Tampa and Hillsborough and Polk Counties, ground water may range from 0.1 to 0.7 ppm. Most readings in unpolluted areas range from 0.0 to 0.2 ppm.

The test for phosphates is accomplished with a Spec-20 spectrophotometer with an infrared tube and filter. The complex that allows this determination is formed as follows:

> Ammonium molybdate reacts with phosphate in an acid medium to form molybdophosphoric acid. This acid is reduced by stannous chloride to form a molybdenum blue complex proportional to the amount of phosphate present.

Reagents and Materials:

1. Spec-20 with IR tube and filter
2. Acid-washed glassware
3. phenolphthalein indicator- dissolve 5 g phenolphthalein in 500 ml 95% ethyl alcohol or isopropyl alcohol and add 500 ml distilled water. Then add 0.02M NaOH until a faint pink color appears.
4. Strong Acid Solution- slowly add 300 ml of concentrated H_2SO_4 to about 600 ml distilled water. When cool add 4.0 ml concentrated HNO_3 and dilute to 1 liter.
5. ammonium molybdate reagent- dissolve 25 g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 175 ml distilled water. Cautiously add 280 ml concentrated H_2SO_4 to 400 ml distilled water. Cool, add the molybdate solution, and dilute to one liter.
6. stannous chloride reagent- dissolve 2.5 g of fresh, dry $SnCl_2\cdot 2H_2O$ in 100 ml glycerol. Heat in a water bath and stir with a glass rod to hasten dissolution. This reagent is stable and requires neither preservation nor special storage.
7. standard phosphate solution- dilute 100.0 ml stock phosphate solution to 1 liter with distilled water. 1.00 ml = 50.0 µg PO_4.

8. stock phosphate solution- dissolve in distilled water 0.7165 g anhydrous potassium dihydrogen phosphate, KH_2PO_4, and dilute to 1 liter. 1.00 ml = 0.500 mg PO_4.

Procedure:

A. Prepare calibration curve between 0 and 50 µg PO_4.

1. the directions for the preparation of calibration curves are found in the users manual of the Spec-20. Use the KH_2PO_4 as the standard.

B. Determine the mg/l PO_4 as P from the sample and calibration curve.

1. Add 50 ml of sample to a 100 ml volumetric flask.
2. Add 1 drop phenolphthalein indicator. If the solution turns pink add strong acid solution dropwise to discharge the color.
3. Dilute to 100.0 ml with distilled water.
4. Add 4.0 ml molybdate reagent and mix thoroughly.
5. Add 10 drops of the stannous chloride reagent and mix thoroughly.†
6. Read the absorbance at 690 mµ, after 10 minutes but before 12 minutes.
7. Calculate mg/l PO_4 as P from the calibration curve and the original sample volume.

† The rate of color development and the intensity of color depends on time and temperature. Samples and standards should be maintained within 2°C of one another. Time can best be controlled by utilizing a timer and adding the stannous chloride at 1 minute intervals and reading the absorbance of each successive sample at 1 minute intervals.

CHLORIDES

Theory:

Chloride can be titrated with mercuric nitrate because of the formation of soluble, slightly dissociated mercuric chloride. In the pH range 2.3-2.8, diphenyl carbazone indicates the endpoint of this titration by formation of a purple complex with excess mercuric ions.

In this method a specific mixture of nitric acid and diphenylcarbazone is added to a water sample, automatically adjusting the pH of most waters to 2.5 ± 0.1. A third substance in this alcoholic mixture, xylene cyanol FF, is used as a pH indicator and a background color to facilitate endpoint detection. The introduction of 10 mg sodium bicarbonate to both the blank and standard titration provides a pH of 2.5 ± 0.1 when 1.0 ml indicator-acidifier reagent is added.

Reagents and Materials:

1. Standard sodium chloride, 0.0141N- dissolve 0.8241 g NaCl (dried at 140°C) in chloride free water and dilute to 1 liter. 1.00 ml = 0.500 mg Cl.
2. Indicator-acidifier reagent- dissolve in the order named 0.25 g diphenylcarbazone, 4.0 ml concentrated HNO_3, and 0.03 g xylene cyanol FF in 100 ml of 95% ethyl alcohol or isopropyl alcohol. Store in a dark bottle in a refrigerator. This reagent is not stable indefinitely. Deterioration causes a slow end-point and high results.

   Inasmuch as pH control plays a critical role in this method, the pH of highly alkaline or acid samples should be adjusted to 2.5 ± 0.1 with 0.1N nitric acid or sodium hydroxide, not with sodium bicarbonate. A pH meter with a non-chloride type of reference electrode should be used

for the pH adjustment. If the usual chloride-type reference electrode is the only type available, the amount of acid or alkali required to achieve a pH of 2.5 ± 0.1 should be determined and this particular sample portion should be discarded. A separate sample portion should then be treated with the determined amount of acid or alkali and the analysis continued in the prescribed manner. Under these circumstances, the nitric acid should be omitted from the acidifier-indicator reagent to maintain the proper pH.

3. Standard Mercuric Nitrate Titrant, 0.0141N.

   Dissolve 2.3 g $Hg(NO_3)_2$ or 2.5 g $Hg(NO_3)_2 \cdot H_2O$ in 100 ml distilled water containing 0.25 ml concentrated HNO_3. Dilute to just under one liter. Perform a preliminary standardization by following the procedure described below. Use replicates containing 5.00 ml standard NaCl solution and 10 mg $NaHCO_3$ diluted to 100 ml with distilled water. Adjust the mercuric nitrate titrant to exactly 0.0141N and perform a final standardization. Store away from the light in a dark bottle. Standard mercuric nitrate titrant, exactly 0.0141N, is equivalent to 0.500 mg Cl per 1.00 ml.

4. sodium bicarbonate, powder

5. special reagents for pH adjustment-

   a. nitric acid, 0.1N. Dilute 6.4 ml concentrated HNO_3 to 1 liter with distilled water.

   b. sodium hydroxide- 0.1N. Dissolve 4.0 g NaOH in distilled water and dilute to 1 liter.

Procedure:

A. Standardization of the mercuric nitrate.

1. Add 1.0 ml of indicator-acidifier reagent to exactly 100.0 ml of sample prepared as described in part 3 of reagents and materials.

   The color of this solution should be green-blue at this point. A light green color indicates a pH of less than 2.0; a pure blue indicates a pH of more than 3.8. For most waters the pH after this addition will be 2.5 ± 0.1. When highly alkaline or acidic waters are encountered, a preliminary pH adjustment to about pH 8 will be necessary before the indicator-acidifier reagent is added. Use the reagents described in step 5 of the reagent and materials section.

2. Titrate the treated sample with mercuric nitrate titrant to a definite purple endpoint. The solution will turn from green-blue to a blue a few drops from the end-point.
3. Perform a blank determination as in step 2 above by titration of 100 ml of distilled water containing 10 mg $NaHCO_3$.
4. Adjust the normality of the mercuric nitrate to exactly 0.0141 by either dilution or by adding more mercuric nitrate.

B. Determine the mg/liter Cl in the sample of water.

1. Use exactly 100.0 ml sample.
2. Add 1.0 ml of the indicator-acidifier reagent to the

sample. The color of this solution should be green-blue at this point. A light green color indicates a pH of less than 2.0; a pure blue indicates a pH of more than 3.8. For most waters the pH after this addition will be 2.5 ± 0.1. When highly alkaline or acidic waters are encountered, a preliminary pH adjustment to about pH 8 will be necessary before the indicator-acidifier reagent is added. Use the reagents described in step 5 of the reagent and materials section.

3. Titrate the treated sample with mercuric nitrate titrant to a definite purple end-point. The solution will turn from green-blue to a blue a few drops from the end-point.
4. Perform a blank determination as in step 2 above by titration of 100 ml of distilled water containing 10 mg $NaHCO_3$.
5. Calculate the mg/liter Cl.

$$\text{mg/l Cl} = \frac{(A-B) \times N \times 35{,}450}{\text{ml sample used}}$$

A = ml used for titration

B = ml used for titration of blank

N = normality of $Hg(NO_3)_2$.

mg/liter NaCl = mg/liter Cl X 1.65

OXYGEN, DISSOLVED

Theory:

Adequate dissolved oxygen (DO) is necessary for the life of fish and other aquatic organisms. The DO concentration may also be associated with corrosivity of water, photosynthetic activity and septicity.

The sample should be collected in a narrow-mouth, glass stoppered bottle of 300-ml capacity. Special precautions are required to avoid entrainment or dissolution of atmospheric oxygen. Allow the bottle to overflow two or three times its volume and replace the stopper, so that no air bubbles are entrained.

This particular method is used for most sewage, effluents, and streams, especially if they contain more than 0.1 mg/l nitrite nitrogen and not more than 1 mg-l ferrous iron.

Reagents:

1. Manganese sulfate solution- Dissolve 480 g $MnSO_4 \cdot 4H_2O$, 400 g $MnSO_4 \cdot 2H_2O$ or 364 g $MnSO_4 \cdot H_2O$ in distilled water, filter, and dilute to 1 liter. The manganese sulfate solution should liberate not more than a trace of iodine when added to an acidified solution of potassium iodide.
2. Alkali-iodide-azide solution- Dissolve 500 g sodium hydroxide, NaOH (or 700 g potassium hydroxide, KOH), and 135 g sodium iodide, NaI (or 150 g potassium iodide, KI), in distilled water and dilute to 1 liter. To this solution add 10 g sodium azide, NaN_3, dissolved in 40 ml distilled water. Potassium and sodium salts may be used interchangeably. This reagent should not give a color when diluted with water and acidified.

3. Sulfuric acid, concentrated- The strength of this acid is about 36N. Therefore, 1 ml is equivalent to about 3 ml of the alkali-iodide-azide solution.

4. Starch solution- Prepare an emulsion of soluble starch in a mortar or beaker with a small quantity of distilled water. Pour this emulsion into 1 liter of boiling water, allow to boil for a few minutes, and let settle over night. Use the clear supernate. This solution may be preserved with 1.25 g salicylic acid per liter or by the addition of a few drops of toluene.

5. Sodium thiosulfate standard solution, 0.025N.
Prepare this solution by dissolving 6.205 g $Na_2S_2O_3 \cdot 5H_2O$ in freshly boiled and cooled water and diluting to 1 liter. Standard sodium thiosulfate solution may be preserved by adding 5 ml chloroform or 0.4 g NaOH per liter. Standard sodium thiosulfate solution, exactly 0.025N, is equivalent to 0.200 mg DO per 1.00 ml.

Procedure:

A. Standardize the sodium thiosulfate solution.

1. Standard potassium biniodate solution, 0.025N-
A stock solution equivalent in strength to 0.1N thiosulfate solution contains 3.249 g/l $KH(IO_3)_2$. The biniodate solution equivalent to the 0.025N thiosulfate contains 0.8124 g/l $KH(IO_3)_2$ and may be prepared by diluting 250 ml stock solution to 1 liter.

Standardization: Dissolve approximately 2 g KI, free from iodate, in an erlenmeyer flask with 100 to 150 ml distilled water; add 10 ml of

10% H_2SO_4 (1 ml H_2SO_4 + 9 ml H_2O), followed by exactly 20.00 ml standard biniodate solution. Dilute to 200 ml and titrate the liberated iodine with the thiosulfate titrant, adding starch toward the end of the titration, when a pale straw color is reached. Exactly 20.00 ml 0.025N thiosulfate should be required when the solutions under comparison are of equal strength. It is convenient to adjust the thiosulfate solution to exactly 0.0250N.

2. Standard potassium dichromate solution, 0.025N. Potassium dichromate may be substituted for biniodate. A solution equivalent to 0.025N sodium thiosulfate contains 1.226 g/l $K_2Cr_2O_7$. The $K_2Cr_2O_7$ should be previously dried at 103°C for 2 hours, and the solution should be prepared in a volumetric flask.

   Standardization: Same as with biniodate, except that 20.00 ml standard dichromate solution is used. Place in the dark for 5 minutes, dilute to approximately 400 ml, and titrate with 0.025N thiosulfate solution.

B. Determine the dissolved oxygen in water sample.

1. To the sample as collected in a 300-ml bottle add 2 ml manganese sulfate solution followed by 2 ml alkali-iodide-azide reagent, well below the surface of the liquid. Stopper with care to exclude air bubbles and mix by gentle

inversion of the bottle several times. When the precipitate settles, leaving a clear supernatant above the manganese hydroxide floc, shake again.

When settling has produced at least 100 ml clear supernate, carefully remove the stopper and immediately add 2.0 ml concentrated H_2SO_4 by allowing the acid to run down the neck of the bottle, restopper, and mix by gentle inversion until dissolution is complete. The iodine should be uniformly distributed throughout the bottle before decanting the amount needed for titration. This should correspond to 200 ml of the original sample after correction for the loss of sample by displacement with the reagents has been made. Thus, when a total of 4 ml (2 ml each) of the manganese sulfate and alkali-iodide-azide reagents is added to a 300-ml bottle, the volume taken for titration is 203 ml.

2. Titrate with 0.025N thiosulfate solution to a pale straw color. Add 2 ml freshly prepared starch solution and continue the titration to the first disappearance of the blue color.
3. Calculate the DO in the water sample.

   1. Because 1 ml 0.025N sodium thiosulfate titrant is equivalent to 0.2 mg DO, each milliliter of sodium thiosulfate titrant used is equivalent to 1 mg/liter DO if a volume equal to 200 ml of original sample is titrated.

2. If the results are desired in milliliters of oxygen gas per liter at $0^{o}C$ and 760 mm Hg pressure, multiply mg/liter DO by 0.698.

REFERENCES

All of the tests and determinations found in this booklet are presented in "Standard Methods for the Examination of Water and Wastewater", 12th or 13th editions. Prepared by the following:
American Public Health Association,
American Water Works Association, and
Water Pollution Control Federation.

Published by the American Public Health Association,
1740 Broadway, New York, N.Y. 10019.
Editor: Herbert P. Orland

Shorter and more concise versions are availably, Methods for Chemical Analysis of Water and Wastes, obtainable from the Orange County Department of Pollution Control. Methods for Chemical Analysis of Water and Wastes, which may by obtained from the Environmental Protection Agency, Washington, D.C.

APPENDIX A

Because we are dealing with analytical tests, the chemicals and equipment used should be of the highest quality. For this reason, when ordering chemicals, choose only the highest purity, preferrably ACS purity or as high purity as possible. Also, be sure to choose only anhydrous reagents as the additional water will lead to erroneous results.

Below is a sample order of the special reagents, chemicals and equipment that will probably be needed before these tests may be performed. This list is not intended to be an actual order, rather an example of the specific things to be ordered with respect to quantity, purity, size, and quality. This sample order is taken from the Fisher Scientific Co. catalog from 1974. This particular catalog was chosen because it contained all of the necessary equipment and chemicals. In some cases it may be necessary to order from more than one supply house in order to obtain all of the chemicals you need.

name	page no.	quantity	catalog no.
mercury(ic) nitrate	1120	¼ lb.	M-168
bromophenol blue	970	5 g.	B-392
diphenyl carbazone	1054	5 g.	D-86
monoethanolamine	1060	1 qt.	M-251
EDTA	1215	¼ lb.	S-311
eriochrome black T	1060	25 g.	E-512
manganese sulfate	1118	1 lb.	M-113
sodium azide	1212	¼ lb.	S-227

potassium iodide	1187	½ lb.	P-410
sodium thiosulfate	1222	1 lb.	S-446
potassium bi-iodate	1183	½ lb.	P-190
ammonium molbydate	938	½ lb.	A-674
antimony potassium tartrate	944	1 lb.	A-865
ascorbic acid	946	5 oz.	A-61
potassium phosphate, monobasic	1189	1 lb.	P-285
potassium acid phthalate	1186	½ lb.	P-243
stannous chloride	1227	1 lb.	T-142
crucibles, Gooch top dia. 32 mm bottom dia. 20 mm	539	30	8-195C
BOD bottles, 300 ml.	519	5	2-926
glass fiber filter paper	392	1 box	9-901A
Spec-20 IR tube and filter.	185	1	7-144-10

These quantities were estimated for a class of 30 students, with each student doing two determinations for each test.

APPENDIX B

Sampling Techniques:

Sampling of lakes is best accomplished by the use of a homemade plexiglass sampler. The sampler is designed to be filled from the bottom to the top. This is done by having the water enter the sampler at the top and flowing through a tube to the bottom. The air in the sampler is forced out at the top through an air vent hole.

Samples are obtained with the plexiglass sampler which is lowered to the two feet from the bottom level and then slowly brought to the surface. This allows a small amount of sample to be obtained from all depths and composited into one large sample that is representative of the lake.

The dissolved oxygen sample is taken directly into the 300 ml bottles from about two feet below the surface. Care must be taken to allow the water to flow into the bottle at a rate that is slow enough so that absolutely no bubbling occurs. If some bubbling does occur then more oxygen will have been dissolved by the water and the sample will be invalid.

Stream samples are obtained in exactly the same manner as the lake composite sample. If the water is too shallow to permit the use of the plexiglass sampler, a surface sample is obtained with a bucket.

Field information obtained and recorded at the time of sampling is as follows:

a. location (in detail)

b. time

c. temperature (in °C)

d. color of the body of water being sampled

e. odor of the sample

f. various weather conditions

g. condition of water (clear, turbid, etc.)

h. approximate flow rate (measured with a cork and watch)

i. any other comments or observations that may be of value.